

UDC 666.112.2:666.122.2:532.73

CALCULATION OF SiO_2 DIFFUSION COEFFICIENTS BASED ON KINETIC CURVES OF SILICA GRAIN DISSOLUTION

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Translated from Steklo i Keramika, No. 4, pp. 13–14, April, 2004.

A method for calculating the SiO_2 diffusion coefficient is proposed and a particular example is described using a generalized kinetic dependence of the process of dissolution of silica grains in melted glass.

The rate of glass formation in a glass melt depends on the intensity of the conversion of bonded silicon dioxide from the surface of dissolving quartz sand grains into the silicate melt and is estimated by the diffusion mass transfer coefficient or, as it is usually termed, the coefficient of SiO_2 diffusion.

The values of SiO_2 diffusion coefficients have been experimentally determined only for some compositions of sodium-silicate glasses in limited temperature intervals that do not cover the regimes of melting impure sodium disilicate in industrial conditions. The experimental methods for determining diffusion coefficients, as a rule, are technically complicated and labor-consuming, especially the methods based on direct measurement of thickness of the boundary diffusion layers formed around dissolving silica grains (the interference method, the radioactive isotope measurement method, x-ray analysis using an electron microprobe, etc.), since they involve special complicated and expensive measuring equipment [1–7].

At the same time, a significant spread is observed in diffusion coefficients of similar melt compositions. These differences can be accounted either by the difference of the methods of analysis used and their different accuracy, or by the degree of correctness of subsequent experimental data processing. The isolated experimental data available in the reference literature [8] are not fit for systematizing and generalizing.

In this context we proposed a method for the calculation of SiO_2 diffusion coefficients using kinetic curves of silica grain dissolution.

Kinetic curves of grain dissolution in the melts of the $\text{Na}_2\text{O} - \text{SiO}_2$ system can be uniquely determined based on a

generalized dependence [9, 10]:

$$m = \bar{\tau}^n; \quad \bar{\tau} = \frac{\tau}{\tau_c}; \quad (1)$$

$$n = 0.05 \exp(3d_0^2) \left(\frac{t}{10^3} \right)^{-7.5};$$

$$\tau_c = 6355 \left(\frac{t}{10^3} \right)^{-10.83} d_0^{0.915} M^{2.717},$$

where m is the part of SiO_2 that has reacted; $\bar{\tau}$ is the relative duration of melting, sec; τ_c is the duration of complete melting of the batch, sec; n is the power index, which is a function of the initial diameter d_0 of SiO_2 particles in the batch, mm, and the melting temperature t , °C; and M is the silica modulus of the batch.

Under the conditions of melting sodium-silicate glasses similar to industrial conditions, the silicate formation stage typically is completed already at $\bar{\tau} = 0.1$; by that moment 90–95% of initial SiO_2 quantity becomes chemical fixed.

Upon passing to the glass formation stage, the rate of dissolution of the residual grains sharply decelerates, stabilizes, and is determined only by diffusion mass transfer.

It is known that the diffusion material flow (kg/sec) for the dissolution of a spherical particle in stationary conditions is found from the expression

$$I = 2\pi d D \Delta\gamma_{\text{SiO}_2}, \quad (2)$$

where d is the particle diameter, m; D is the molecular diffusion coefficient, m^2/sec ; $\Delta\gamma_{\text{SiO}_2} = \gamma_{\text{SiO}_2}^s - \gamma_{\text{SiO}_2}^m$ is the concentration head constituting the difference between SiO_2 concentration on the particle surface and in the surrounding melt, kg/m^3 .

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An ultimate saturation concentration of the melt for a given temperature $\gamma_{\text{SiO}_2}^s$ is found from the solubility diagram of the system.

The material flow is determined based on the material balance of a particle dissolving in the conditions of diffusion mass transfer and is calculated from the expression

$$I = \frac{dm}{d\tau} = 0.5\pi\rho_p d \frac{dd}{d\tau}, \quad (3)$$

where ρ_p is the density of the material of the particle, kg/m^3 .

From joint analysis of expressions (2) and (3) we obtain a calculation formula for the diffusion coefficient:

$$D = \frac{d^2\rho_p}{12\Delta\gamma_{\text{SiO}_2}\tau}. \quad (4)$$

The following assumptions are made in the proposed method for calculating the diffusion coefficient:

- the dissolving particles of quartz sand have a spherical shape;
- the dissolution of particles of the same fraction in glass melt proceeds simultaneously according to the same kinetic curve;
- the delay of the process of homogenization of SiO_2 content dissolved in the melt is not taken into account.

Let us consider a particular example of calculating the diffusion coefficient using the generalized kinetic dependence.

Let us take the reference data from an experimental melting [11, 12], which investigated the process of batch melting of sodium silicate glass with $M = 3.535$ and the initial sand grain size 0.55 mm at a temperature of 1250°C.

The generalized kinetic dependence (1) for the particular melting regime has the following form:

$$m = \bar{\tau}^{0.0232}; \quad \bar{\tau} = \frac{\tau}{10,140},$$

since

$$n = 0.05 \exp(3 \times 0.055^2) \times 1.25^{-7.5} = 0.0232;$$

$$\tau_c = 6355 \times 1.25^{-10.83} d_0^{0.915} M^{2.717} = 10,140 \text{ sec.}$$

Let us arbitrarily fix a point on the kinetic curve segment $\bar{\tau} > 0.1$ (for instance $\bar{\tau} = 0.2$), at which the dissolution process depends only on diffusion mass transfer, and then find the part of SiO_2 that has dissolved:

$$m = 0.2^{0.0232} = 0.963.$$

By that moment the residual sand grains will have the following estimated size:

$$d_{\text{est}} = \sqrt[3]{(1 - 0.963) \times 0.55^3} = 0.183 \text{ mm.}$$

Let us determine the time needed to complete the dissolution of the residual sand grains:

$$\tau_{\text{est}} = 10,140 \times (1 - 0.2) = 8112 \text{ sec.}$$

At the estimated point the homogenized composition of the silicate melt formed upon the dissolution of 96.3% initial silica contains 76.73% SiO_2 , which corresponds to $M = 3.5$.

The SiO_2 concentration in this melt will be

$$\gamma_{\text{SiO}_2}^m = 0.01(\text{SiO}_2)\rho_m = 0.01 \times 76.73 \times 2195 = 1684 \text{ kg/m}^3.$$

The saturation concentration at a temperature of 1250°C is

$$\gamma_{\text{SiO}_2}^s = 0.01(\text{SiO}_2)\rho_{s.m} = 0.01 \times 82.4 \times 2193 = 1807 \text{ kg/m}^3.$$

The concentration head, accordingly, is equal to

$$\Delta\gamma_{\text{SiO}_2} = 1807 - 1684 = 123 \text{ kg/m}^3.$$

The values ρ_m and $\rho_{s.m}$ are determined using the Cohenen [8] data as values inverse to the specific volumes of the melt under the conditions considered.

Using formula (4) we calculated the value of SiO_2 diffusion coefficient for the sodium silicate melt with $M = 3.5$:

$$D = \frac{(0.183 \times 10^{-3})^2 \times 2650}{12 \times 123 \times 8112} = 7.42 \times 10^{-12} \text{ m}^2/\text{sec.}$$

The diffusion coefficient value calculated by us agrees with known experimental data. In particular, the authors of [5], studying the dissolution of vitreous silica in a sodium silicate melt with $M = 2.0$ at 1250°C, obtained the value $D = 7.55 \times 10^{-12} \text{ m}^2/\text{sec.}$

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